New Developments in Long-term Sampling of Dioxins

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Introduction

The emissions of Dioxins and Furans (Polychlorinated Dibenzodioxins and Dibenzofurans, PCDF/Ds) from industrial sources are still one of the most important issues discussed in public, politics and industry. Due to the fact that environmental regulations are on the way to be harmonised in the EU countries, the measurements of those compounds in the stack gas of e. g. waste incinerators will increase. All EU countries now have a stack discharge limit of 0.1 ng TEQ/m³N for hazardous waste incinerators, several countries have this limit for municipal waste incinerators as well.

PCDF/D stack gas samplings at stationary sources are usually performed using a sampling train according to EN 1948, part 1. This allows sampling times between 6 to 8 hours which are also needed to achieve acceptable detection limits in the laboratory GC/MS analysis which follows after collection of the flue gas samples. Usually, 3 samplings are performed at a source during one year.

There often is public concern about the dioxin emissions during the remaining time of about 1,800 hours per year and source. Additionally, the German legislation is demanding the minimisation of dioxin emissions and it also requires to use a long-term measuring system as soon as it is available. Meanwhile, several plants have installed such a system not only in Germany but in other EU countries as well.

Development of a long-term sampling system

In 1990, the company GfA developed an easy-to-handle, simple and low cost dioxin sampling system, the so called „adsorption method" in the scope of a R & D project. This method now is one of the best validated systems for dioxin testing in flue gas and was the first system that fulfilled the requirements of a VDI guideline as to performance characteristics for concentration levels below 0.1 ng TEQ/m³.

Break-through tests of the collection unit of this method clearly showed that sampling periods can be extended from 6 hours to 4 weeks without any significant PCDF/D concentration in a back up collector. Those results were verified for different plant types, dioxin concentration levels and also for other highly volatile, unpolar compounds like PCBs, Chlorobenzenes, Chlorophenols and PAHs.

Based on the „adsorption method" GfA and the company bm - becker messtechnik developed a computer controlled, automatic and easy to handle sampling system called „AMESA" (**A**dsorption **Me**thod for **Sa**mpling of Dioxins

In 1994 AMESA was presented on ACHEMA in Frankfurt. Representatives from industry, authorities and international press were largely interested in long-term dioxin supervision.

Certification tests

In 1996/97, the TÜV Rheinland GmbH in Köln, Germany carried out certification tests with the AMESA system.

Three identical systems were installed at the MSWI in Amsterdam The systems underwent a 6 month field test. During this time more than 150 dioxin samplings and analyses were performed. The analysis covered the flue gas, condensed flue gas water, back-up units, washing solutions and blank values.

The results of the certification tests were published by the TÜV in a detailed report. The main results are summarised here:

- The disposability of the three systems during the test period was 97 %
- The reproducibility $R_D = X/(S_D \times t_{95\%}$ was 5.5 for sampling of 16 hours to 2 weeks and 3.9 for 4 week samplings (R_D = reproducibility from double measurements; X = average value; S_D = standard deviation from double measurements; $t_{95\%}$ = factor at 95 % statistical confidence). All those RD s are higher than required.
- All results from the AMESA samplings are comparable to the results obtained from samplings according to EN 1948. Cross check analysis between different dioxin laboratories were performed as well.
- Breakthroughs after 4 week samplings were 1 – 3 % related to the TEQ value. This is less than the normal standard deviation of the complete method.
- The samples collected in the adsorption unit of AMESA can be stored 5 months until analysis without any loss of PCDF/Ds.

Experiences from operating AMESA systems and conclusions

The discussion about so-called data gaps is growing (i. e. the difference in the Dioxin concentrations found in ambient air or other environmental samples like soil and the emissions measured at different industrial plants). The EU commission is planning to perform more nation-wide measuring programs to identify those missing sources, but also to get more data overall.

The AMESA system is now installed at several municipal and hazardous waste incinerators in Germany and Belgium. After 5 municipal waste incinerators in Belgium were closed in late 1997, the Flanders government ordered that those plants can only go back to operation after installation of a long-term Dioxin sampling system.

It is known that start-up and shut-down periods can also cause higher dioxin emissions than regular. Also possible so-called memory effects in wet scrubbers equipped with certain polymer material can occur which can result in increased dioxin emissions after certain periods of time. It is possible that those effects can not be observed during normal 6 hour dioxin sampling periods. The AMESA system can help to detect those possible accumulations of dioxins in the plant.

The AMESA system is now used for the following purposes:

- Acceptance of the incineration plant by the public and the local governments;
- Acceptance of low cost air pollution control equipment by the government if the Dioxin emissions are monitored long-term;
- Reduction of the incineration temperature at hazardous waste incinerators if it can be proved by long-term Dioxin measurements that the emissions do not exceed the limit of 0.1 ng TEQ/m^3.

References

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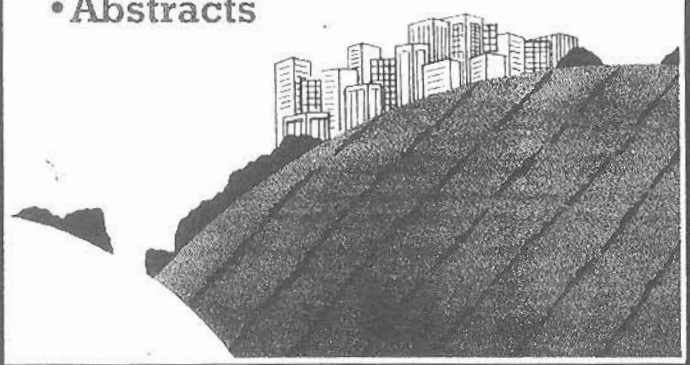

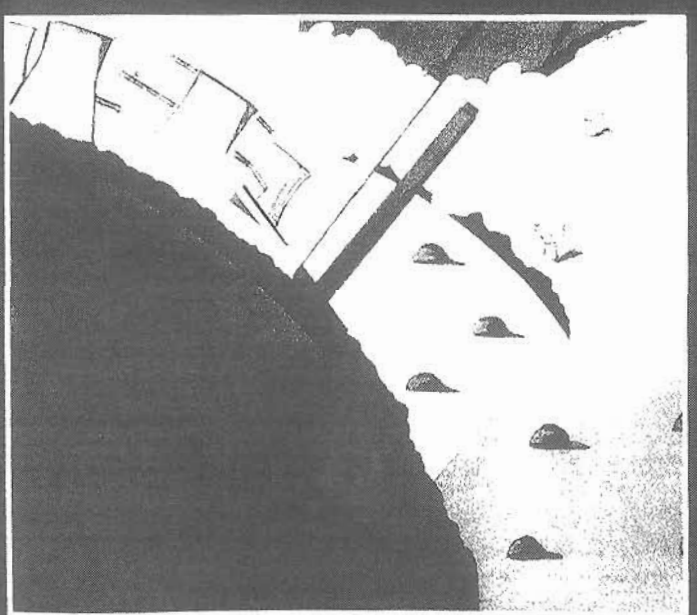

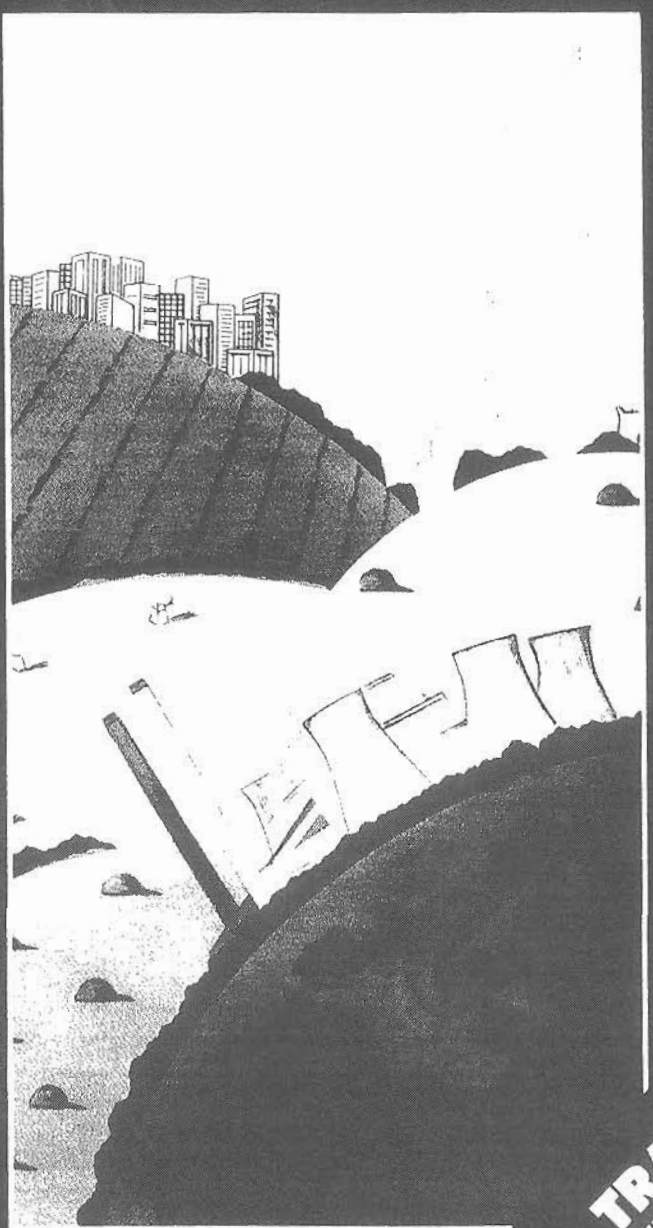

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